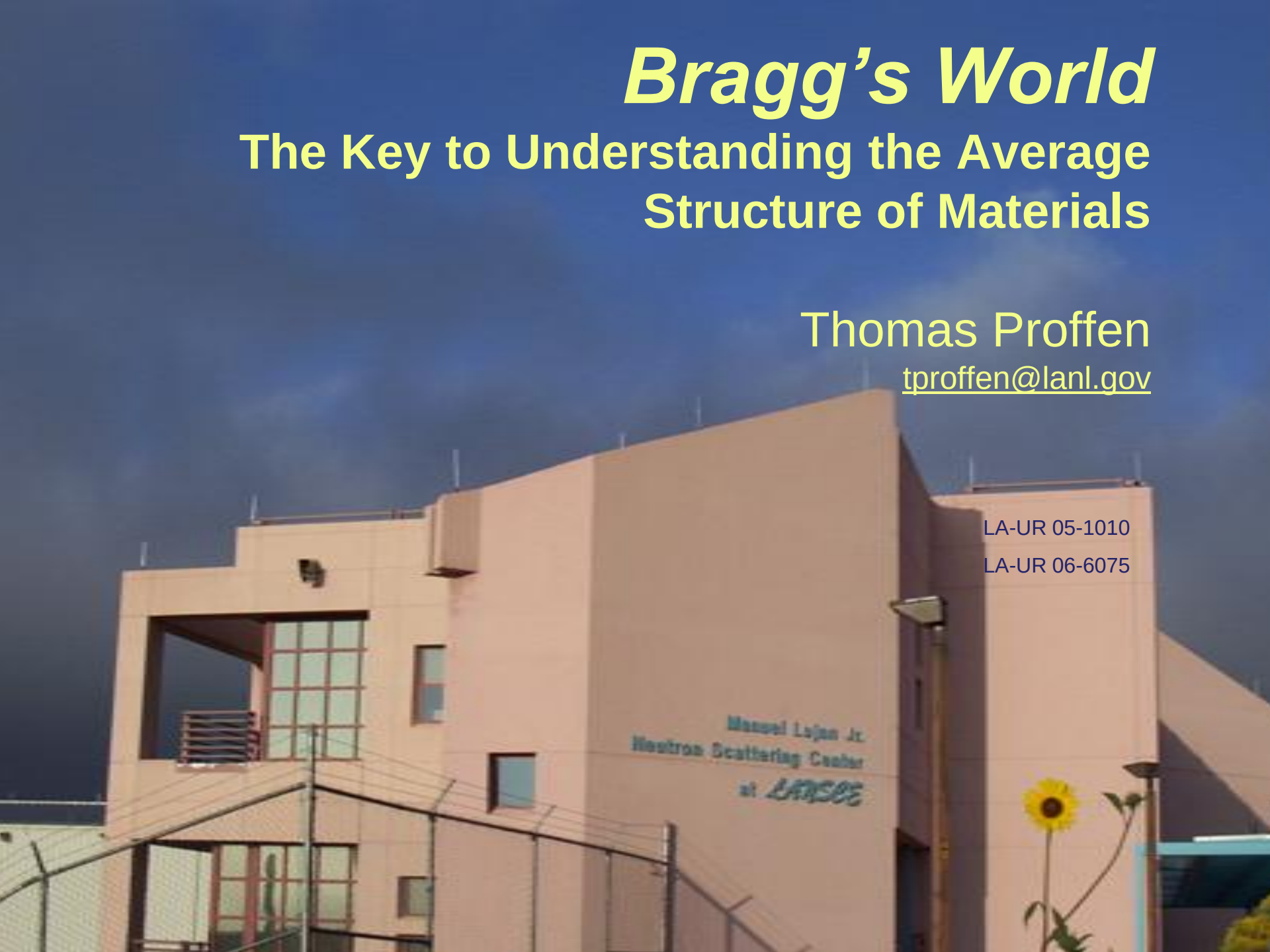
Bragg's World

The Key to Understanding the Average Structure of Materials

Thomas Proffen
tproffen@lanl.gov

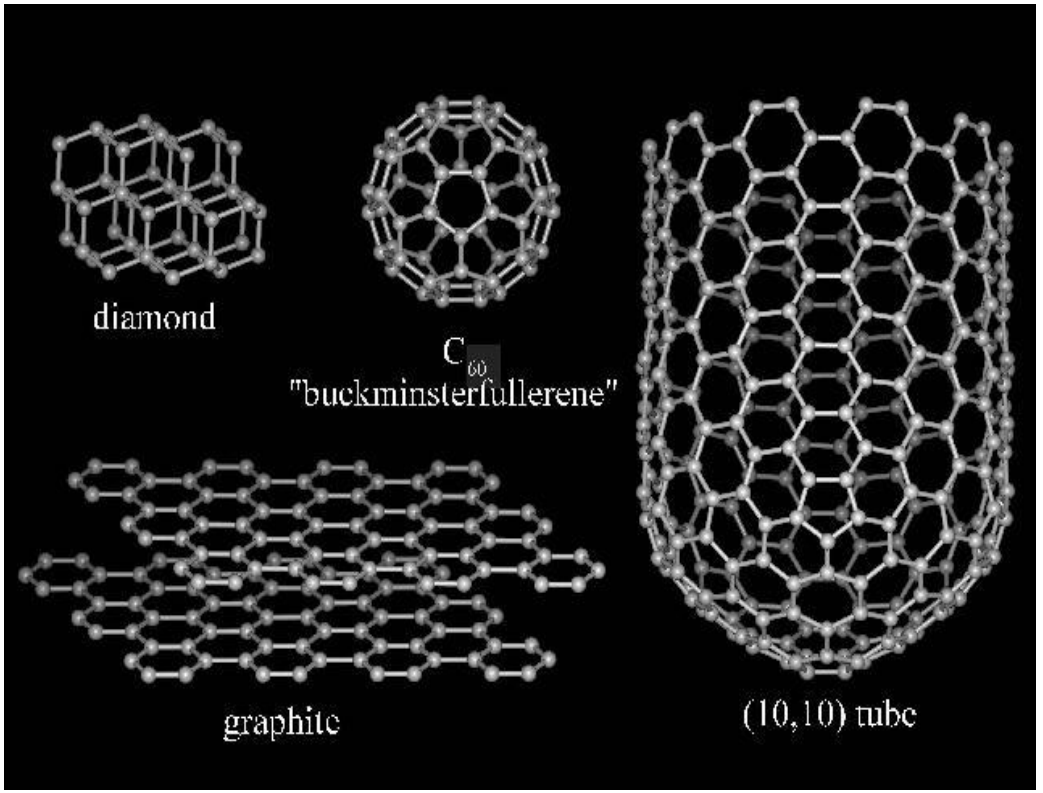
LA-UR 05-1010
LA-UR 06-6075



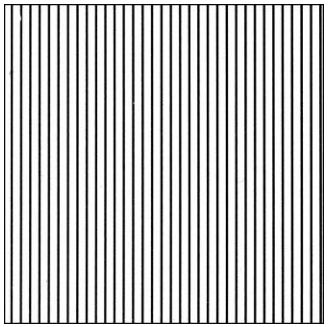
Why do we care about the atomic structure?

The atomic structure has a profound influence on the properties of materials. Consider carbon ...

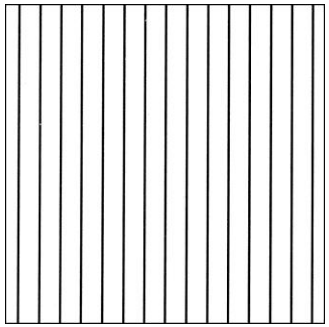
- Diamond
  - hard
  - transparent
  - insulating
  - expensive
- Graphite
  - soft
  - black
  - metallic
  - cheap



Diffraction in action

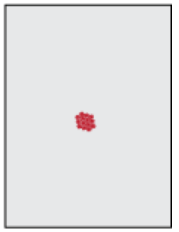


1a: narrow

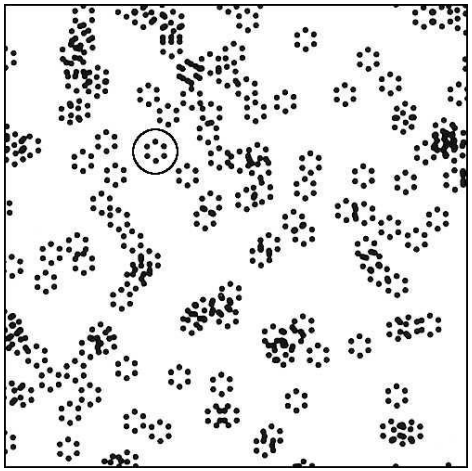


1c: wide

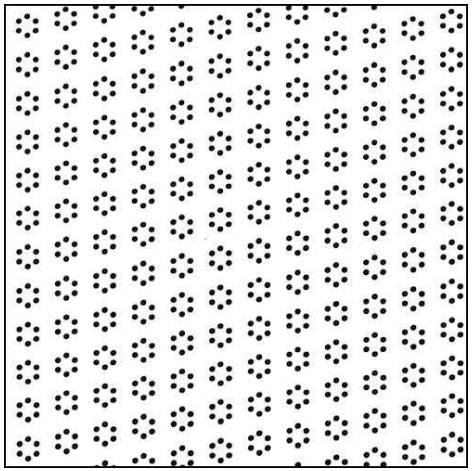
Example 1:
Diffraction grating



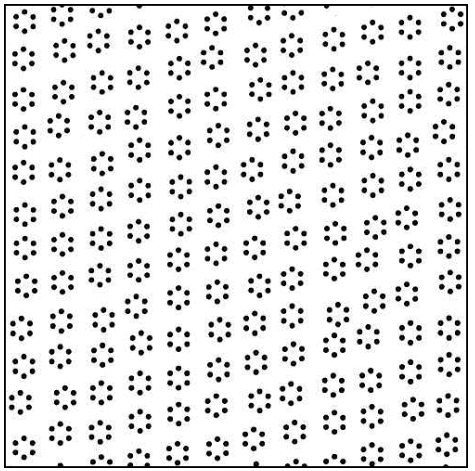
Example 2:
Benzene molecules



8a: random



8d: lattice



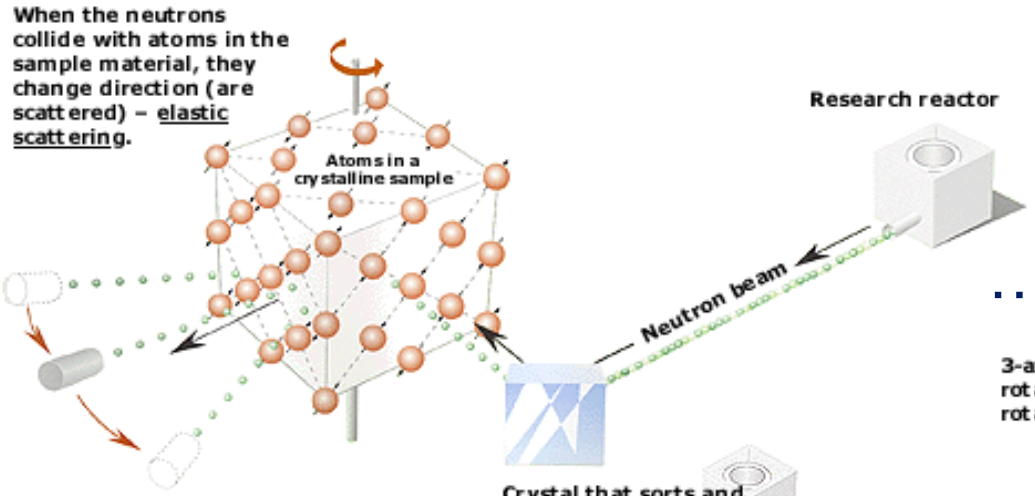
8e: lattice with disorder (TDS)

http://rsc.anu.edu.au/~welberry/Optical_transform/

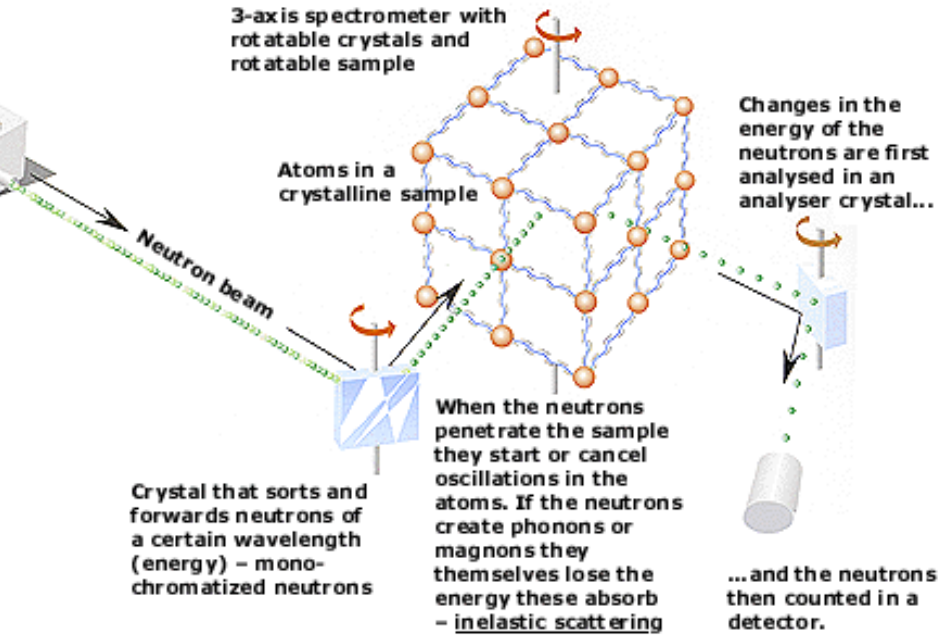
How about using Neutrons ?

The 1994 Nobel Prize in Physics – Shull & Brockhouse

Neutrons show where the atoms are….

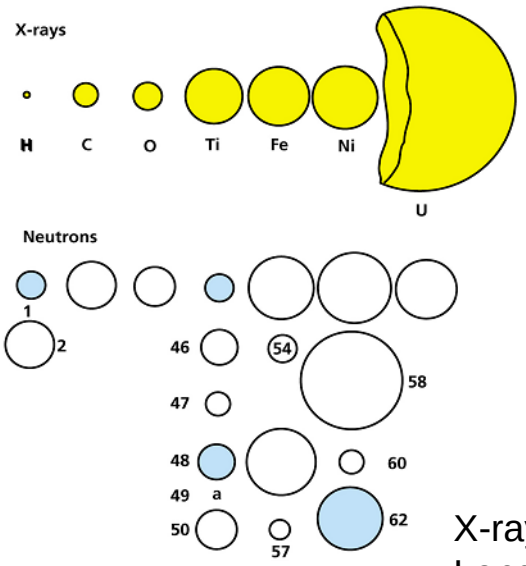


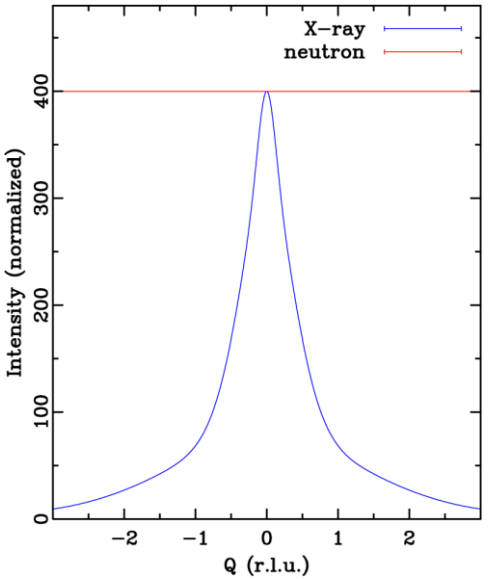
…and what the atoms do.



Why use neutrons ?

- Sensitive to light atoms (e.g. H)
- Contrast by isotope substitution
- Easy sample environment (T,p,..)
- No ‘formfactor’ (good for PDF)
- Weak ⇒ large samples & long measuring times ..





Scattering from single atom

X-ray and neutron scattering Lengths for selected elements.

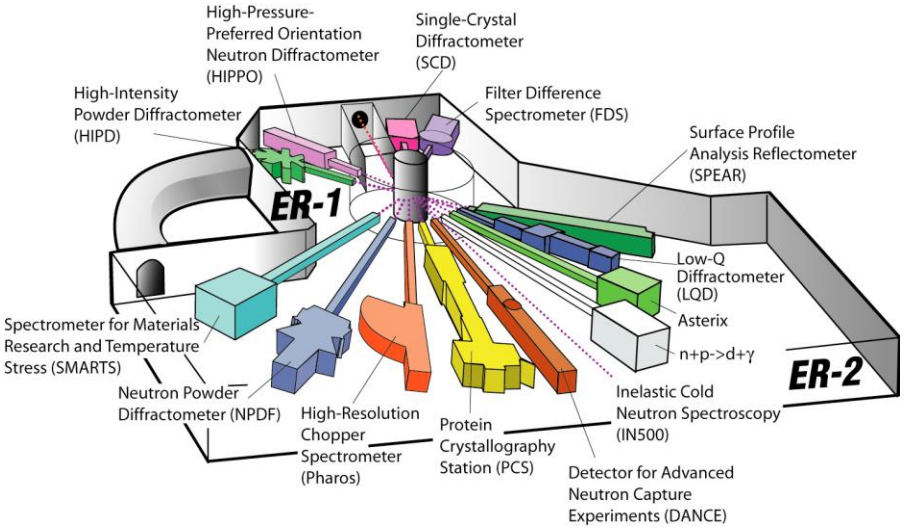
Elastic, coherent, inelastic, incoherent ??

- The intensity of elastic, coherent neutron scattering is proportional to the spatial Fourier Transform of the Pair Correlation Function, G(r)
  I.e. the probability of finding a particle at position r if there is simultaneously a particle at r=0

- The intensity of inelastic coherent neutron scattering is proportional to the space *and time* Fourier Transforms of the *time-dependent* pair correlation function function, G(r,t) = probability of finding a particle at position r *at time t* when there is a particle at r=0 and *t=0*.

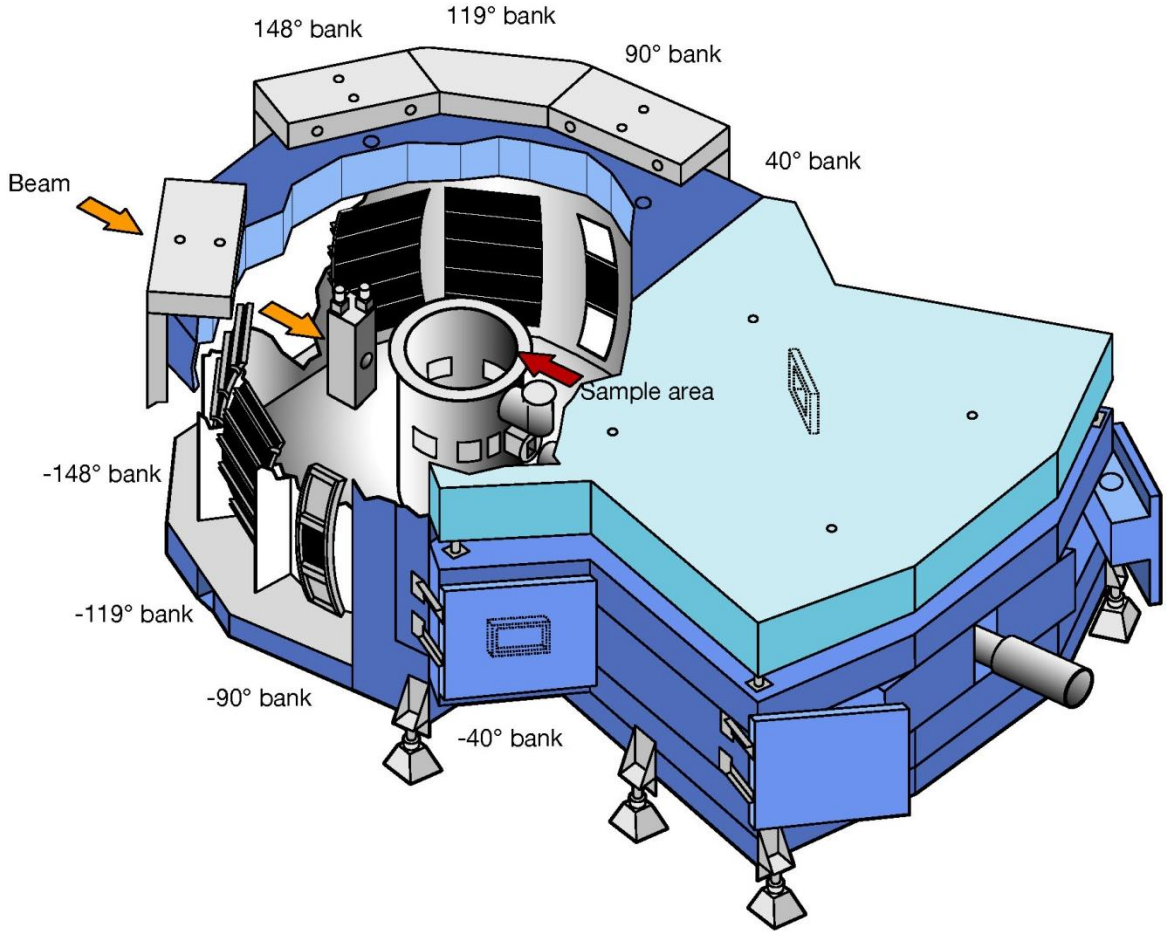
- For inelastic *incoherent* scattering, the intensity is proportional to the space and time Fourier Transforms of the *self-correlation* function, $G_s(r,t)$, i.e. the probability of finding a particle at position r at time t when *the same* particle was at r=0 at t=0

The instrument NPDF

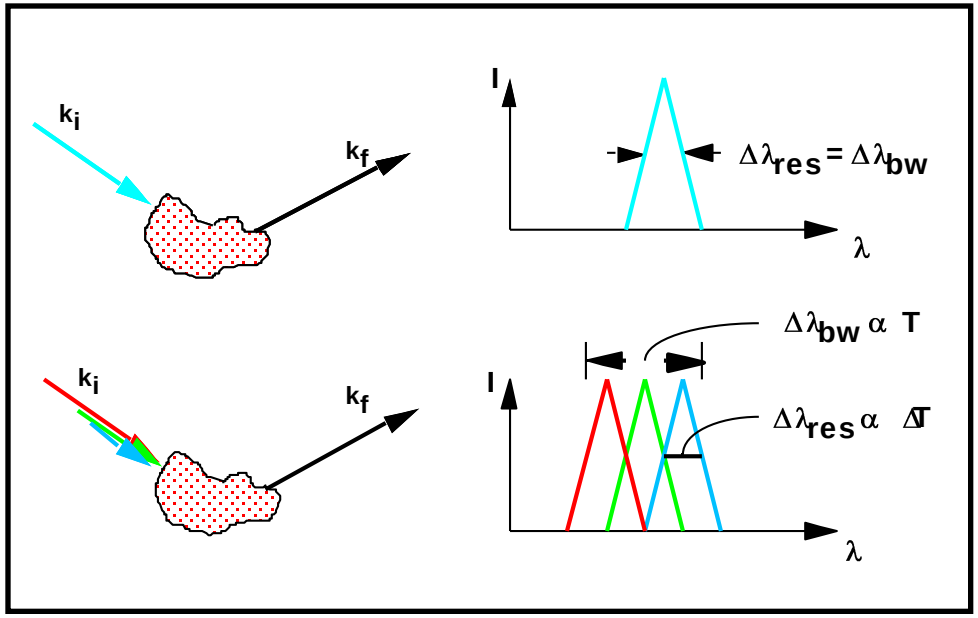


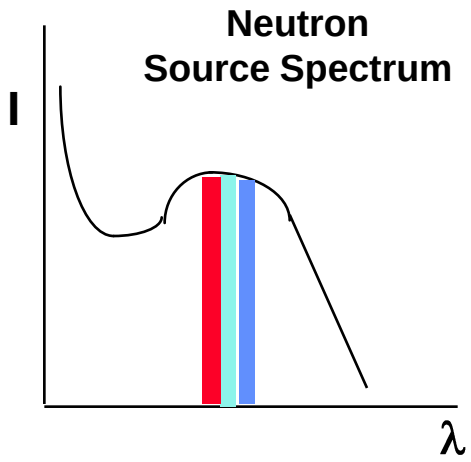
NPDF
Flightpath 1

NPDF: Neutron Powder Diffractometer



Time of Flight Diffraction





Angle dispersive: Vary scattering angle in Bragg's law
Energy dispersive: Vary wavelength (TOF – wavelength)

Bragg's World
Or
Finding the average structure

World of Crystallography
Lecture A. Wills (Wed)

Bragg's world: Structure of crystals

The Nobel Prize in Physics 1915

"for their services in the analysis of crystal structure by means of X-rays"

Sir William Henry Bragg

1/2 of the prize

United Kingdom

London University
London, United Kingdom

b. 1862
d. 1942

William Lawrence Bragg

1/2 of the prize

United Kingdom

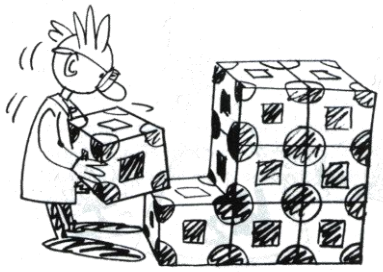
Victoria University
Manchester, United Kingdom

b. 1890
(in Adelaide, Australia)
d. 1971

Bragg's law

$$n\lambda = 2d \sin\theta$$

- Assumes periodicity
- Average structure from Bragg peak positions and intensities



unit cell

The repeating unit of a crystal.

Bragg's world: Theory

The condition for a Bragg-peak to appear is:

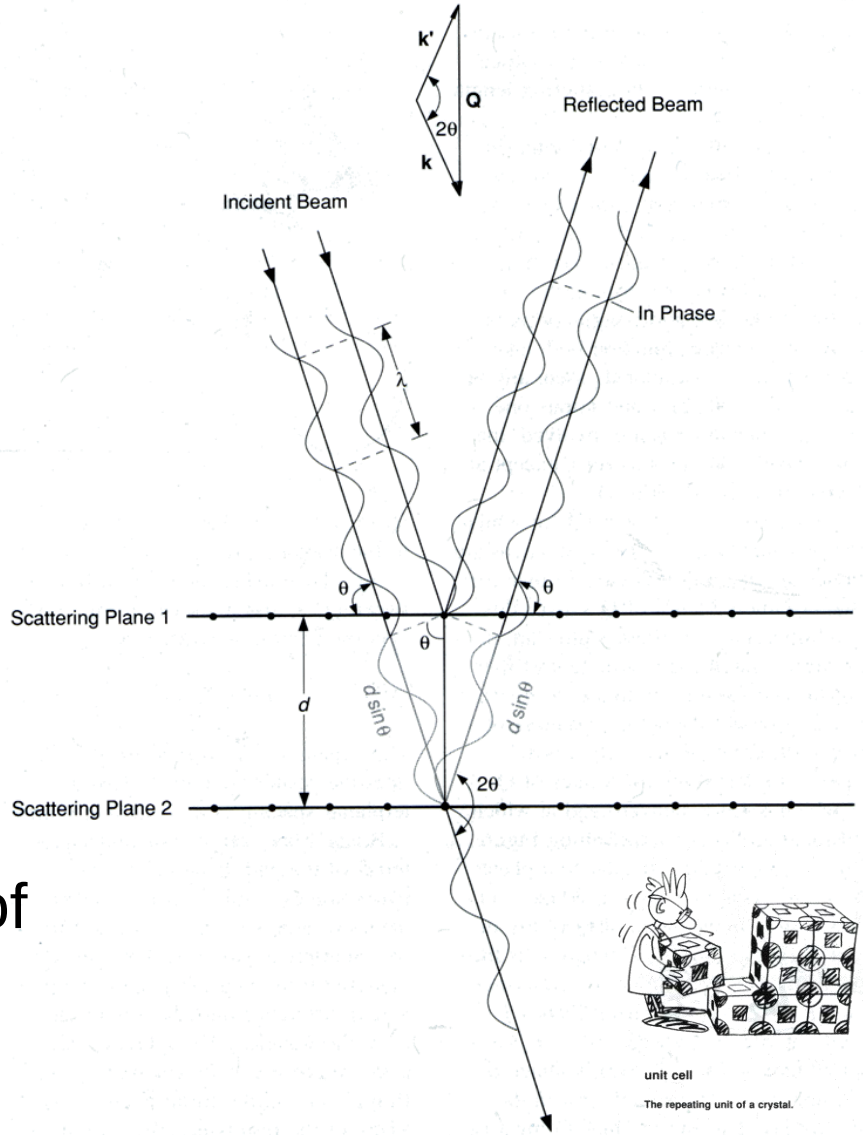
$$n\lambda = 2d \sin\theta$$

or

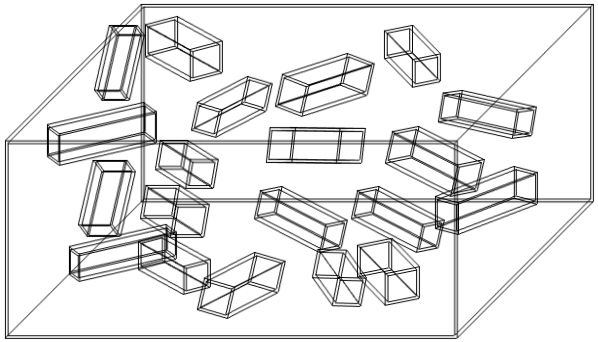
$$\mathbf{Q} = \mathbf{k} - \mathbf{k}' = \mathbf{K}_{hkl}$$

$$F_{\mathbf{K}} = \sum_i b_i e^{i\mathbf{Q}.\mathbf{r}_i}$$

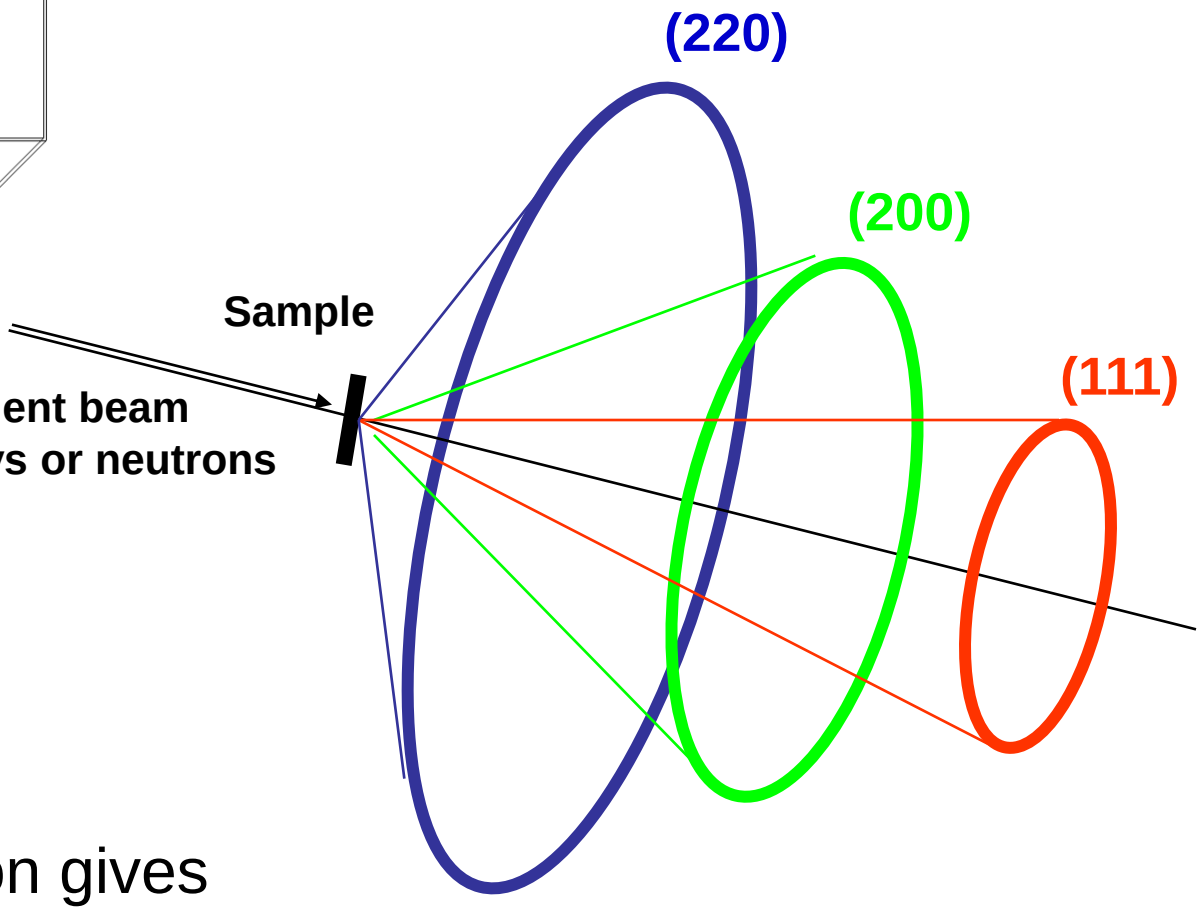
The intensity of the Bragg peak is given by the square of the "Structure factor":



Bragg's world: Powder Diffraction



All orientations of crystallites possible.



Powder Diffraction gives Scattering on Debye-Scherrer Cones

Rietveld refinement technique

$$I_c = I_o\{\Sigma k_h F^2_h m_h L_h P(\Delta_h) + I_b\}$$

I_o - incident intensity - variable for fixed 2Q

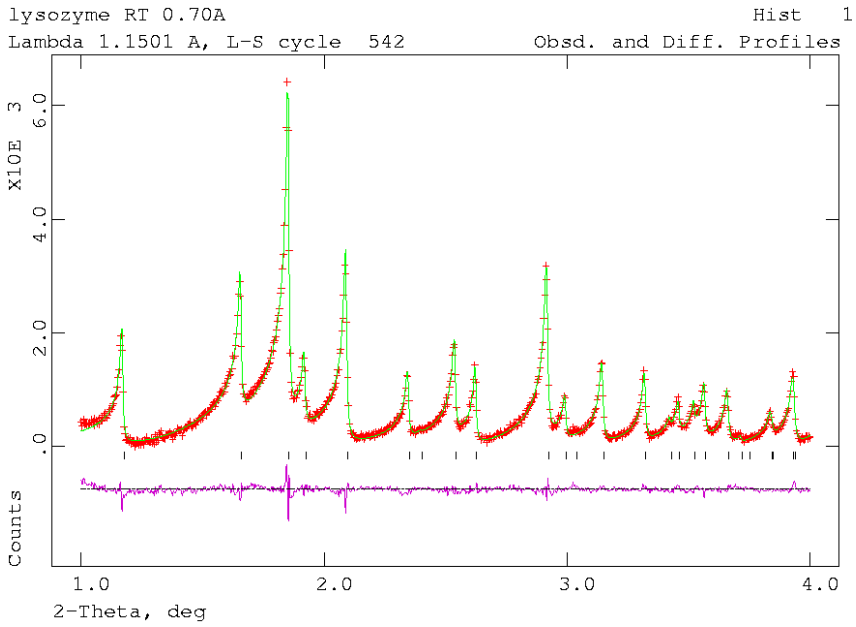
k_h - scale factor for particular phase

F^2_h - structure factor for particular reflection

m_h - reflection multiplicity

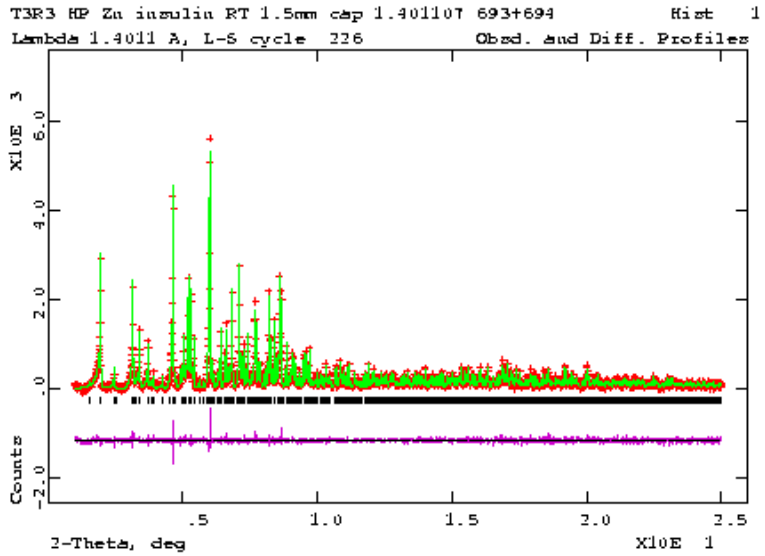
L_h - correction factors on intensity - texture, etc.

$P(D_h)$ - peak shape function – includes instrumental resolution, crystallite size, microstrain, etc.

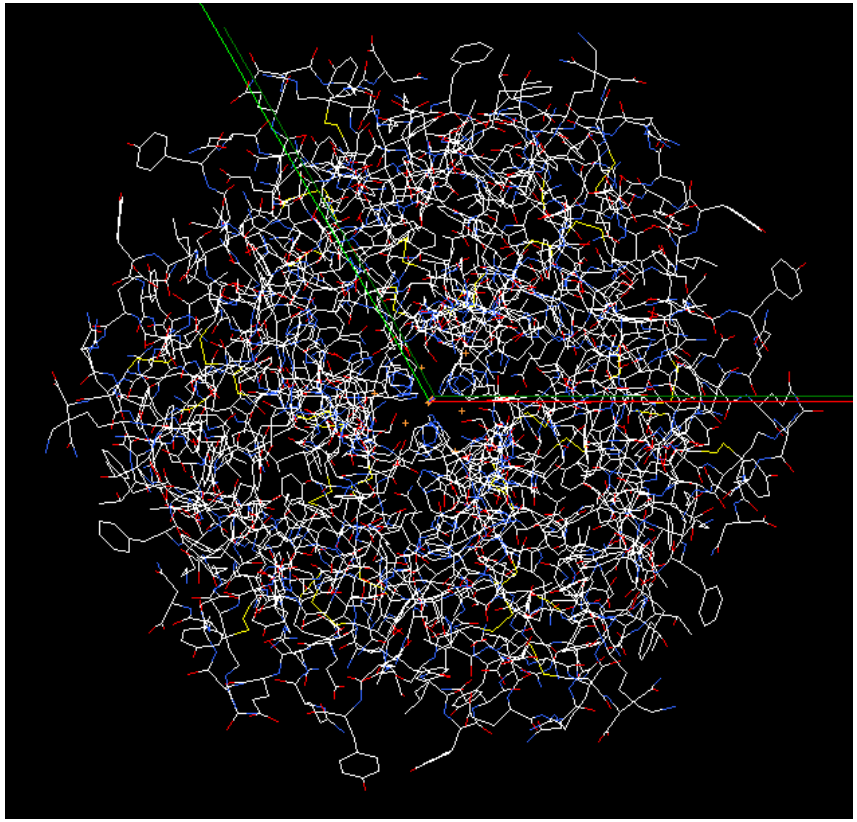


Learn more in HIPD practical ..

Structure from powder diffraction



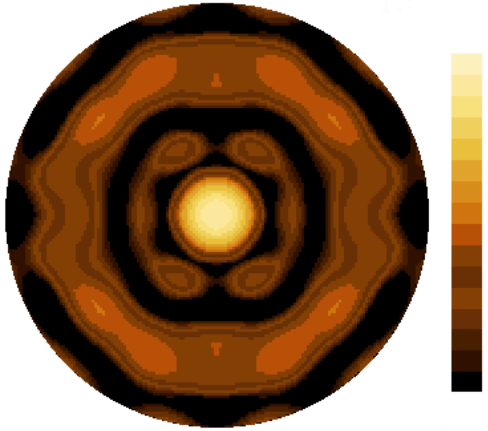
Determination of the atomic structure using diffraction has revolutionized our knowledge about how materials work ..



- Zn insulin structure (> 1600 atoms in unit cell) determined from powder diffraction data (R.B. van Dreele)
- Average structure determined using Bragg reflections.

Bragg's world: Beyond the average structure

- Bragg profiles: size, size distribution and shape of crystallites, and strain.
- Intensity along powder rings: texture and preferred orientation.



Texture of Ti wire plate (Lujan Center)

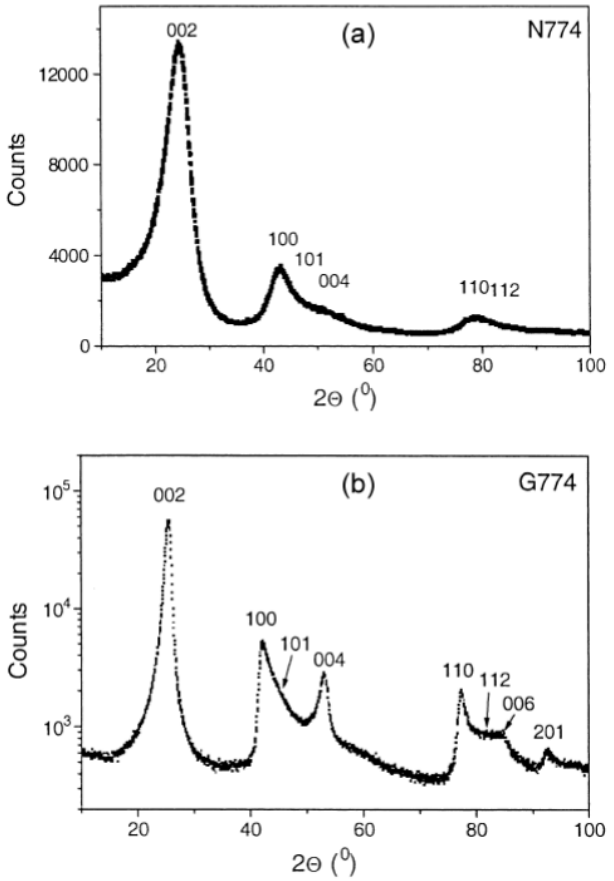


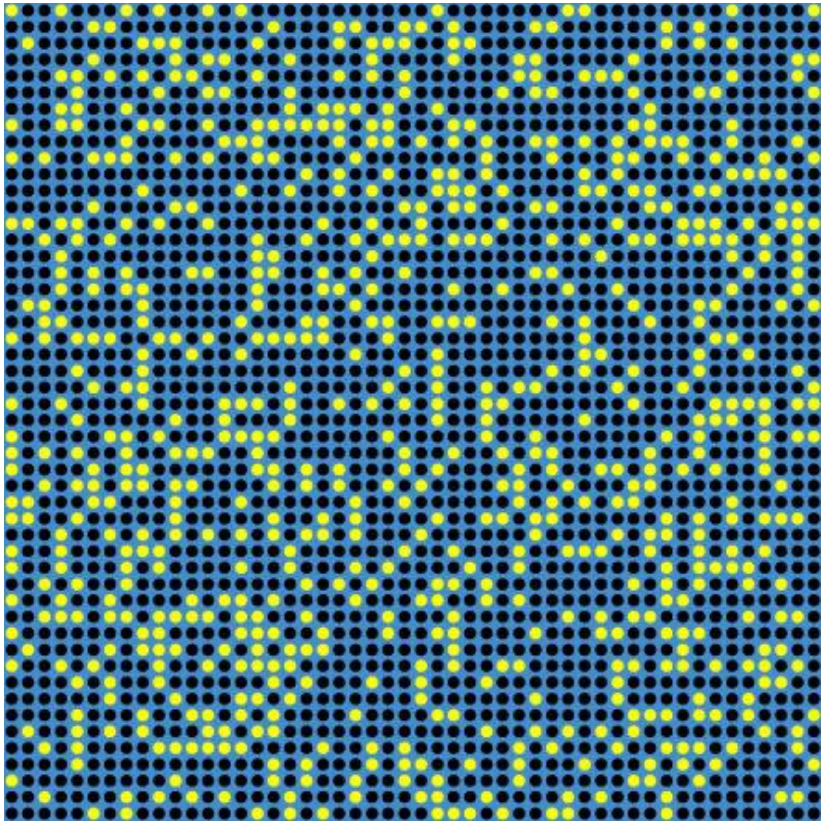
Fig. 1. The powder diffractograms for the N774 carbon black specimen in the initial state (a) and for the specimen G774 after annealing at 2700°C (b). The intensity in logarithmic scale in (b) shows details of low intensity peaks.

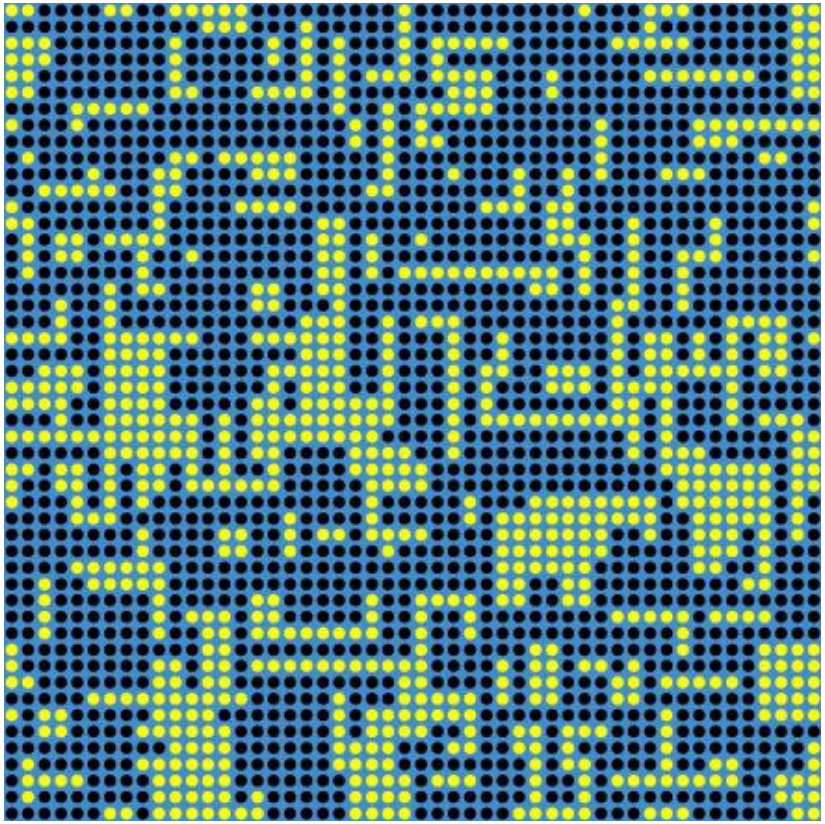
From Ungár, et al, *Carbon* **40,** 929 (2002)

Beyond Bragg ??

Total scattering
Lecture (Tue)

Total scattering ?

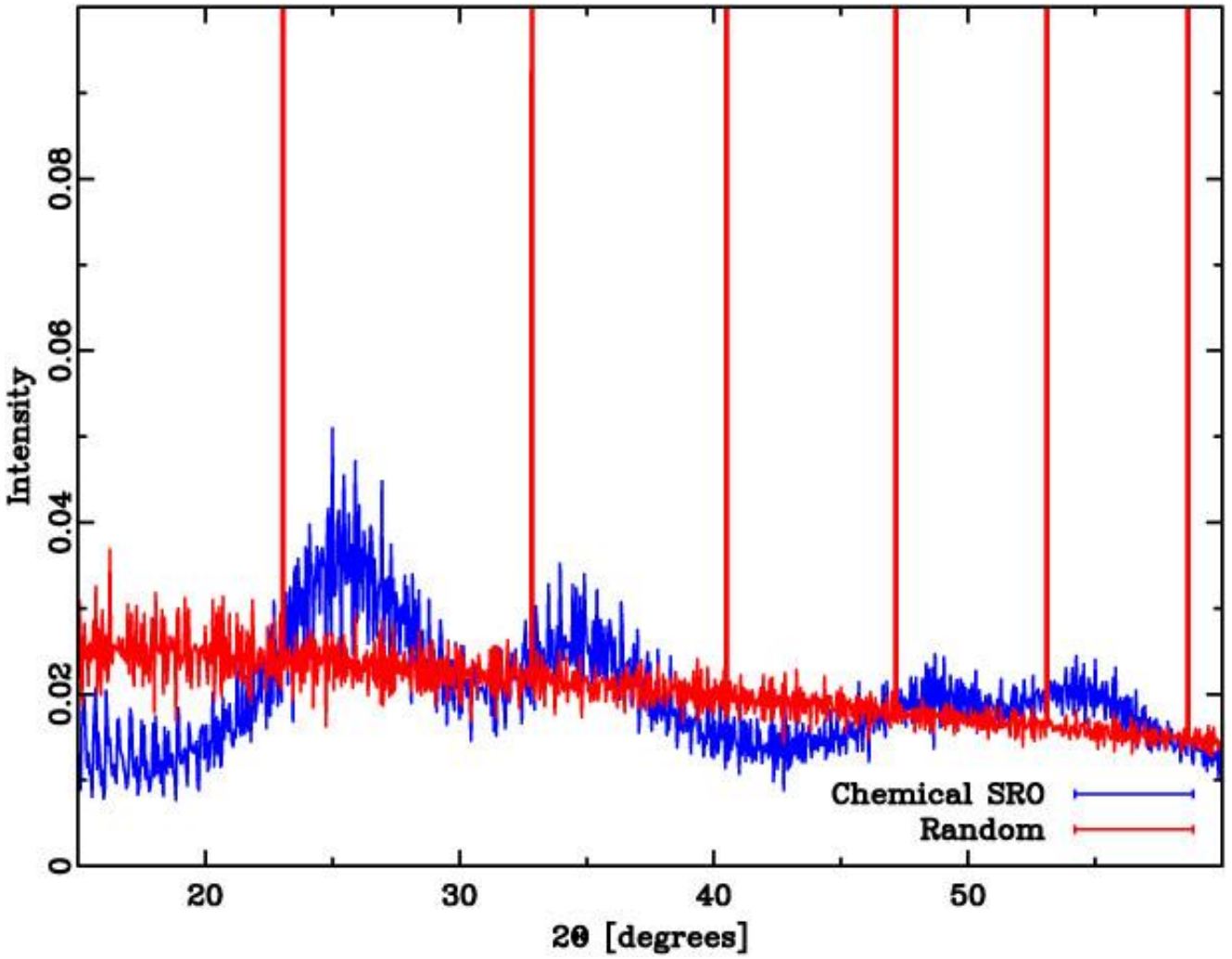




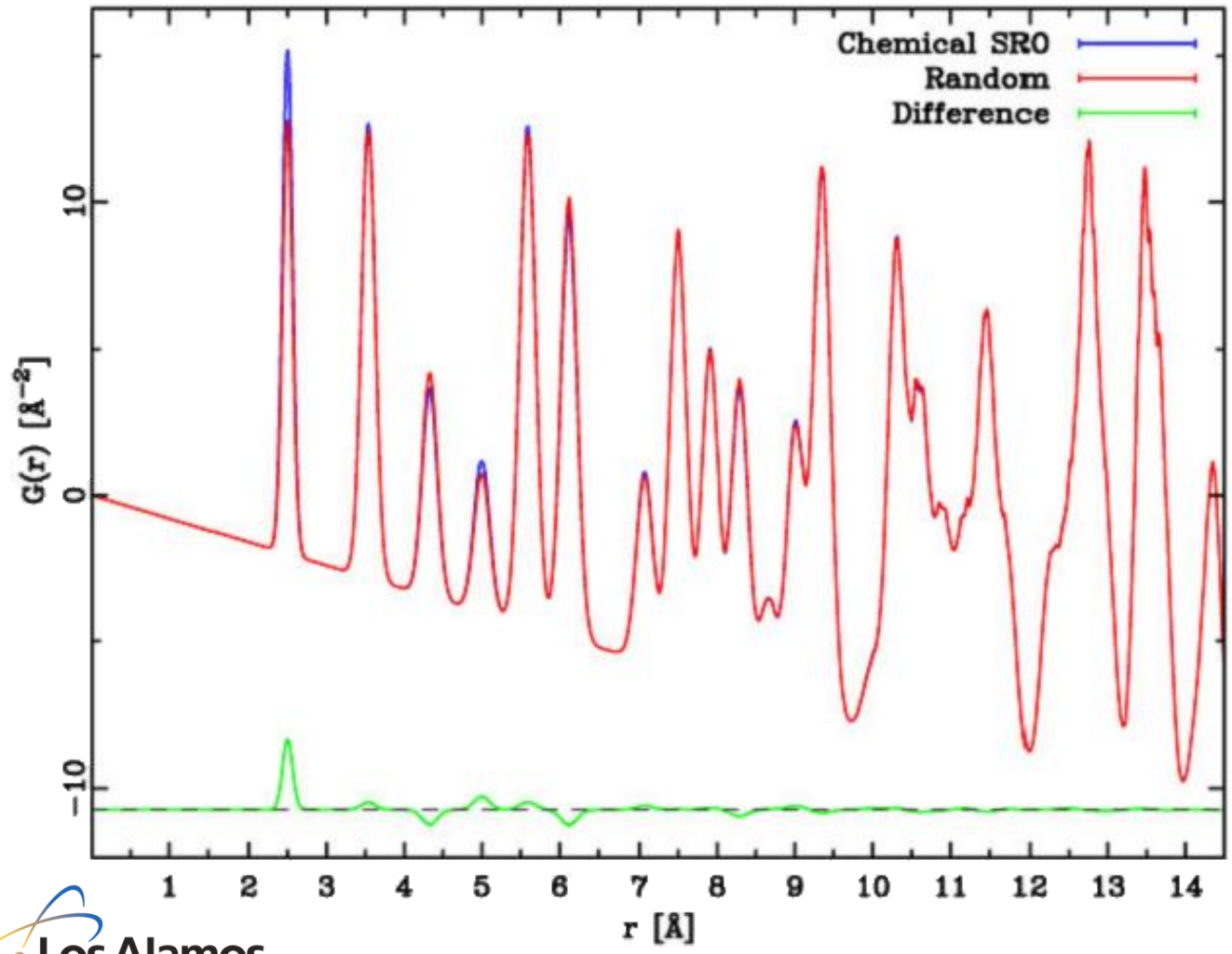
Cross section of 50x50x50 u.c. model crystal consisting of 70% black atoms and 30% *vacancies* !

Properties might depend on vacancy ordering !!

How about powder diffraction ?



Finally the Pair Distribution Function (PDF)



The PDF is the Fourier transform of the total scattering diffraction pattern !

Proffen, *Z. Krist*, **215**, 661 (2000)

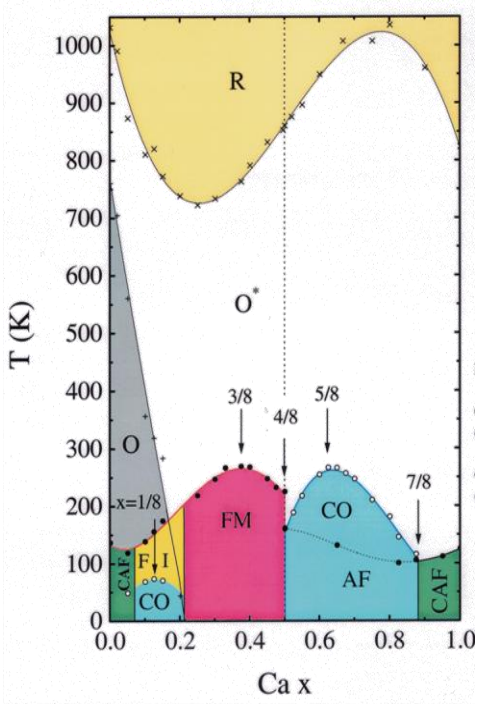
Example:

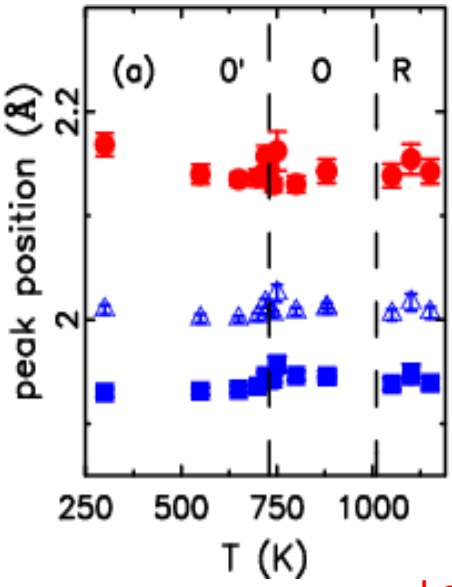
Local structure in $La_xCa_{1-x}MnO_3$

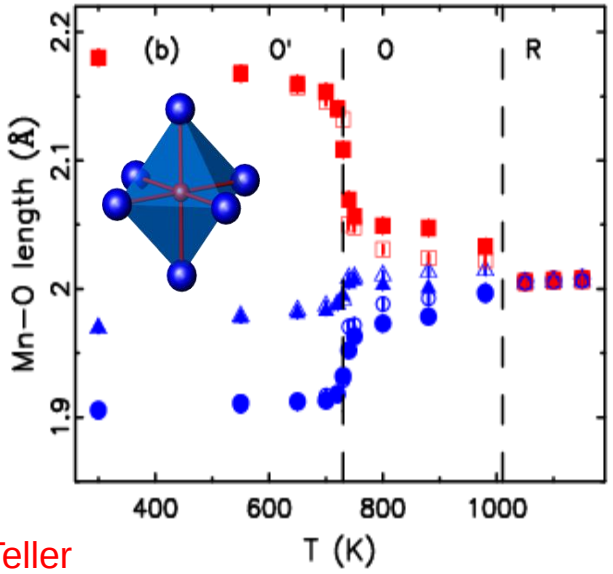
Simon Billinge
Emil Bozin
Xiangyn Qiu

Thomas Proffen

$LaMnO_3$: Jahn-Teller distortion







Jahn Teller
Long Mn-O bond

Local structure

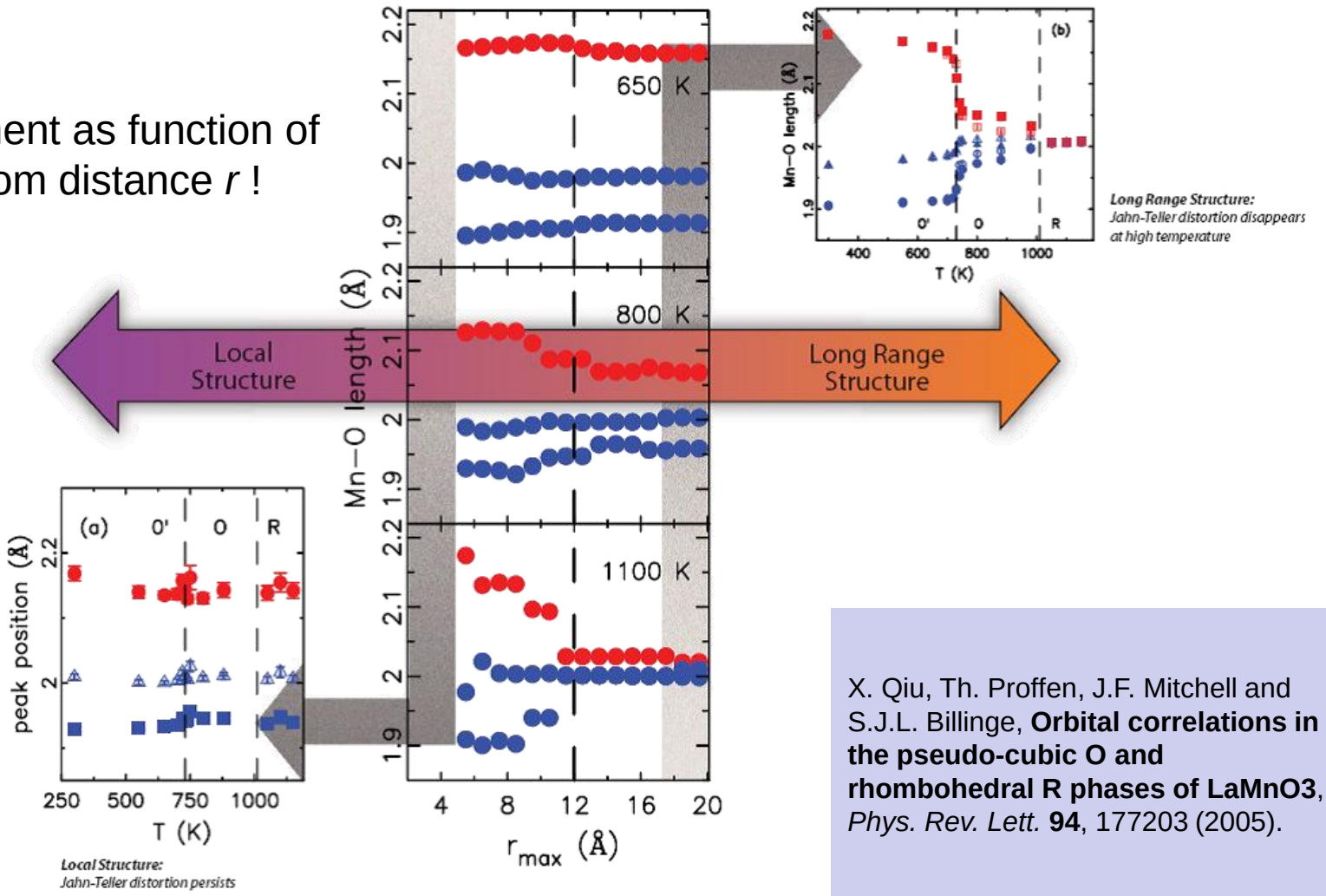
Average structure

- Mn-O bond lengths are invariant with temperature, right up into the R-phase
- JT distortions persist locally in the pseudocubic phase
- Agrees with XAFS result: M. C. Sanchez et al., PRL (2003).

DISTORTED OR NOT DISTORTED?

Study of the Jahn-Teller distortion in $LaMnO_3$

Refinement as function of atom-atom distance *r* !



X. Qiu, Th. Proffen, J.F. Mitchell and S.J.L. Billinge, **Orbital correlations in the pseudo-cubic O and rhombohedral R phases of LaMnO3**, *Phys. Rev. Lett.* **94**, 177203 (2005).


Thank you
LANSCE